STUDIES ON THE SHRINKAGE PHENOMENON: VIII. EFFECT OF PRETANNING PROCESSES ON AREA SHRINKAGE AND RECOVERY

K. J. KEDLAYA, N. RAMANATHAN & Y. NAYUDAMMA
Central Leather Research Institute, Madras

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A study of the effect of each chemical treatment involved in beamhouse operations on the hydrothermal shrinkage and area recovery properties of goat skin is presented. It is observed that raw skins (soaked) possess better hydrothermal stability, shrink more and recover less in the area compared to the limed samples. On deliming, the reverse trend is observed, i.e., area shrinkage and hydrothermal stability are increased and recovery is decreased On pickling of delimed samples, the shrinkage temperature and area shrinkage are lowered and recovery is enhanced. If pickled samples are shrunk in the pickle medium, the shrinkage temperature is increased, the area shrinkage is increased and recovery considerably decreased.

A good deal of work has been done on shrinkage temperature,[1-8] linear,[9, 10] area,[11, 12] volume[13] and apparent volume[14] shrinkage behaviour of hide, skin and leather. But no study has been made on the area and apparent volume changes accompanying shrinkage of hides and skins subject to pretanning operations. Since pretanning beamhouse operations viz., soaking, liming, deliming and pickling influence the final characteristics of the leathers, a systematic study was carried out to find out the effect of each pretanning operation on the area and apparent volume shrinkage and recovery of goat skin. Data on the area shrinkage and recovery are reported here.

Experimental

It was reported by Nayudamma *et al.*[11] that area shrinkage depends on the location of the specimen in the hide or skin. Hence, in choosing the samples, an attempt was made to eliminate the influence of locational variation. The scheme of cutting out samples illustrated in Fig. 1

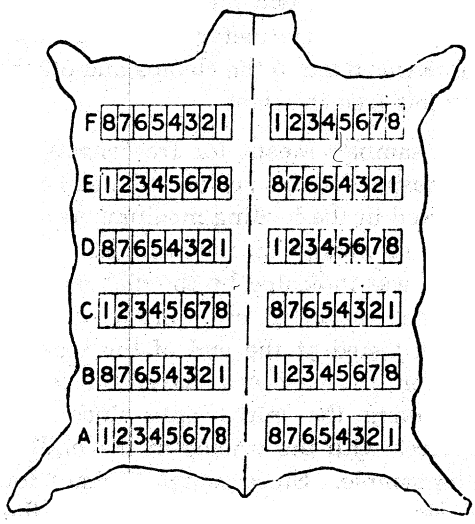

FIG. 1

is based on the fact that two adjacent samples on a skin or hide show less variation than any other pair.[15] For instance, in one block one sample was obtained from the region near the backbone whereas in the adjacent block a sample was obtained near the belly region. After the next chemical treatment, samples adjacent to these samples were used for finding out the effect of treatment given on the area shrinkage. The samples marked 1, 2, 3 and 4 were tested after the soaking, liming, deliming and pickling operations respectively. The samples marked 5, 6, 7 and 8 were used for the stages involved in chrome tanning, results of which are to be reported separately.

Method for determining the area shrinkage and the shrinkage temperature

The outline of the wet samples before shrinkage, after shrinkage and after recovery in water overnight was traced on a translucent paper after placing the sample between two micro glass slides.[11] A Theis shrinkage meter was used. One sample was fixed to the clamps and others were left free in water.

The samples meant for free shrinkage were suspended in a perforated metal cage immersed in the heating medium. As soon as the shrinkage of the samples under tension was indicated by the dial reading, the cage was lifted out. In the case of samples tested at the end of the soaking operation, the hair was shaved off before determining the initial area since hair interferes with the tracing of the outline of the sample. Since samples meant for free shrinkage were removed from the heating medium as soon as the sample under tension exhibited shrinkage, the shrinkage would not have been complete (referred here as 'partial' shrinkage). In order to know the behaviour of completely shrunken samples, another set of samples was subjected to complete shrinkage and area shrinkage and recovery of completely shrunken samples were determined. The area shrinkage and recovery were calculated as

$$\% \text{ area shrinkage} = \frac{x_1 - x_2}{x_1} \times 100$$

$$\% \text{ area recovery} = \frac{x_3 - x_2}{x_1 - x_2} \times 100$$

where x_1 is area before shrinkage, x_2 is area after shrinkage and x_3 area after recovery.

Partial area shrinkage values of 36 samples and complete area shrinkage values of 24 samples and their averages are given in Tables 1 and 2.

Processing of skin

A pack of goat skins was processed upto pickling. Samples were cut out at the end of every pretanning operation for the shrinkage temperature, area shrinkage and recovery studies. The details of the process are as follows:

Freshly slaughtered goat skins cured for one week are used. On the first day, the skins are soaked for 4 hours and limed with a paint consisting of 1% sodium sulphide and 7% lime (on raw weight) in 12 parts of water. Next day, the skins are unhaired and relimed with 150 parts old lime liquor and 150 parts new lime liquor containing 5% lime (on raw weight). On the third day, they are

Table 1

EFFECT OF PRETANNING PROCESSES ON AREA SHRINKAGE (PARTIAL) AND RECOVERY

Samples	Soaked (No. 1)		Limed (No. 2)		Delimed (No. 3)		Pickled (No. 4)	
	AS	AR	AS	AR	AS	AR	AS	AR
Skin I								
AL	41	15	36	41	44	13	29	33
BL	48	21	30	46	46	5	46*	16*
CL	26	18	30	32	54	17	42	22
DL	41	19	32	23	48	2	52*	8*
EL	40	13	30	24	42	15	44	30
FL	34	13	39	22	45	12	65*	3*
AR	43	3	23	27	57	19	53	33
BR	44	12	21	—	62	24	68*	10*
CR	36	5	22	22	52	10	48	37
DR	46	10	21	23	44	14	51*	3*
ER	40	4	27	19	52	13	44	24
FR	45	5	18	21	53	15	65*	2*
Skin II								
AL	42	4	17	20	53	7	44	36
BL	46	7	33	52	55	5	69*	3*
CL	46	0	30	35	45	12	54	40
DL	38	0	28	11	54	9	60*	2*
EL	44	8	14	45	52	15	57	34
FL	39	0	27	27	49	2	55*	6*
AR	37	10	18	15	40	5	56	31
BR	45	14	23	19	37	16	56*	6*
CR	47	2	18	—	42	13	47	27
DR	44	6	18	24	33	6	80*	2*
ER	46	13	10	66	46	15	49	31
FR	41	6	19	60	49	11	68*	10*
Skin III								
AL	40	13	27	29	52	6	35	32
BL	61	20	19	13	48	16	54*	7*
CL	31	14	25	55	47	2	37	12
DL	23		15	0	39	10	52*	5*
EL	27	3	16	42	39	14	39	25
FL	28	9	21	29	48	12	60*	
AR	31	9	20	29	40	12	41	
BR	36	19	24	46	43	18	57*	7*
CR	42	17	25	39	45	11	39	19
DR	41	0	17	39	30	—	69*	11*
ER	31	14	16	57	50	11	36	
FR	39	18	17	23	42	23	64*	9*
Average value	40	9	23(21)	32(30)	47	11	43(37)	29(20)
							61*(53*)	6*(5*)
T_s(°C)	71		53		62		52(62*)	

AS: Area shrinkage (%); AR: Area recovery (%)

(Figures in the parenthesis relate to AS values accounting for incipient shrinkage)

* Pickled samples shrunk and recovered in pickle medium

again delimed using 5% lime in 300% float (on raw weight). On the fourth day, the stock is delimed with 0·5% ammonium sulphate in 300% float (on pelt weight) and then pickled using 1·5% sulphuric acid and 8% salt in 200% float (on fleshed weight).

Results and discussion

It is seen from Tables 1 and 2 that raw skin possesses better hydrothermal stability, shrinks more in area and recovers less when compared to the limed samples in both the 'partial' and 'complete' shrinkage. But area shrinkage values are less

Table 2

EFFECT OF PRETANNING PROCESSES ON AREA SHRINKAGE (COMPLETE) AND RECOVERY

Samples	Soaked (No. 1)		Limed (No. 2)		Delimed (No. 3)		Pickled (No. 4)	
	AS	AR	AS	AR	AS	AR	AS	AR
Skin I								
AL	60	7	48	35	65	12	65	21
BL	59	3	46	29	76	11	74*	3*
CL	67	4	49	44	62	9	60	19
DL	66	6	55	44	66	15	73*	2*
EL	56	5	42	52	61	17	62	28
FL	58	1	44	45	60	—	66*	6*
AR	60	8	53	25	70	18	62	31
BR	58	9	48	22	72	12	67*	3*
CR	55	3	40	38	68	13	45	41
DR	56	5	46	30	62	18	66*	0*
ER	60	5	55	21	66	17	60	22
FR	54	6	45	30	64	7	69*	0*
Skin II								
AL	58	2	51	26	61	13	56	22
BL	57	6	47	36	69	11	75*	11*
CL	57	10	55	32	65	7	65	26
DL	56	3	53	39	65	2	73*	0*
EL	66	3	54	50	63	16	56	33
FL	61	9	50	28	62	13	71*	0*
AR	57	3	50	39	68	13	56	14
BR	59	5	52	40	64	17	72*	0*
CR	67	2	55	25	55	14	61	13
DR	59	7	52	28	67	24	68*	3*
ER	60	2	42	28	58	15	55	33
FR	59	5	47	57	59	18	66*	4*
Average value	59	6	49(43)	35(26)	65	13	59(51) 70*(61*)	25(19) 3*(2*)

Table 3

INCIPIENT SHRINKAGE CAUSED BY PROCESSING

Sample	% incipient shrinkage due to liming of soaked goatskins	% recovery due to deliming	% incipient shrinkage due to pickling
AL	9	18	18
BL	12	11	—
CL	10	13	16
DL	14	26	12
EL	14	19	11
FL	6	10	9
AR	5	20	21
BR	13	12	—
CR	10	9	16
DR	9	10	9
ER	16	17	17
Average	11	15	13

and the magnitude of variation in values is more in the case of partial shrinkage. Perhaps nonrupture of all crosslinks of H-bond type is responsible for (a) decrease in area shrinkage and increase in area recovery and (b) greater magnitude of variation in partial shrinkage values.

It may be noted that there is an incipient shrinkage* due to swelling and plumping effects of liming. Hence to know the extent of influence of incipient shrinkage, skin samples ($1 \times 2''$) were processed and the change in area was noted. Table 3 shows that the liming causes an incipient shrinkage of 11% and deliming a recovery of 15%. Again shrinkage is noticed to an extent of 13% due to the dehydration effect of pickling. Thus, both the partial and complete area shrinkage values of limed and pickled samples are decreased. For example, average shrinkage values of completely shrunken limed and pickled samples in water are reduced from 49 and 59% to 43 and 51% respectively and those of pickled samples in pickle from 70 to 61%. Area recovery values of shrunken limed and pickled samples are also decreased to a small extent by the incipient shrinkage that occurs due to liming or pickling; yet these values are greater than those of the control or delimed samples. A similar decrease is also noticed in the case of area recovery of pickled samples in pickle (Table 2).

As regards limed samples, plumping and swelling due to liming and the presence of free and/or combined lime retard the area shrinkage and increase the

*Incipient change: shrinkage or recovery $= \frac{I_1 - I_2}{I_1} \times 100$ where I_1 = area of sample due to first treatment, and I_2 = area of sample due to subsequent treatments.

recovery though swelling forces lower the shrinkage temperature.[3] Swelling forces accelerate shrinkage due to weakening or breaking of crosslinks like H-bonds but may not allow the collagen network to shrink beyond a certain limit because of the presence of impediments in the form of free and/or combined lime.

Once the lime is removed by ammonium sulphate in the deliming process, osmotic swelling is completely reduced and the lyotropic effect of plumping is partially reduced.[3] Hence the reverse trend viz., increase in area shrinkage and hydrothermal stability, and decrease in area recovery is observed.

On pickling, shrinkage temperature and percent area shrinkage were lowered and area recovery was increased compared to delimed samples. During the shrinkage in water medium, the salt of the pickled skin would be diluted[3] and consequential swelling[3] would break the cohesive forces, reducing the shrinkage temperature. The swelling forces oppose the shrinkage in dimension, resulting in less area shrinkage. In order to assess the extent of influence of acid swelling caused by dilution, alternate pickled samples were shrunk in the pickle medium. And it was observed that the shrinkage temperature of pickled pelt in pickle was higher than that of the delimed one in water. The absence of swelling during shrinkage and recovery of pickled samples in pickle leads to more area shrinkage and less recovery compared to the values of pickled samples tested in water medium.

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